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TENTH EDITION

Merriam-Webster, Incorporated  
Springfield, Massachusetts, U.S.A.



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First Printing 1993

Library of Congress Cataloging in Publication Data  
Main entry under title:

Merriam-Webster's collegiate dictionary. — 10th ed.

p. cm.

Includes index.

ISBN 0-87779-708-0 (unindexed). — ISBN 0-87779-709-9 (indexed).

— ISBN 0-87779-710-2 (deluxe)

1. English language—Dictionaries. I. Merriam-Webster, Inc.

PE1628.M36 1993

423—dc20

93-20206

CIP

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Made in the United States of America

123456RMcN93

worth two shillings **b**: any of several similar coins issued in Commonwealth countries **3**: GULDEN **4**: FORINT  
**florist** \flōr-ist, flōr-, flār- n (1623): one who sells or grows for sale flowers and ornamental plants — **florist-ry** \flōr-ist-ri/ **n**  
**floristic** \flōr-ist-ik/ **adj** (1898): of or relating to flowers, a flora, or the phytogeographical study of plants and plant groups — **floristic-ally** \flōr-ist-ik-ē/ **adv**

**floruit** \flōr-(y)-wot, flār- n [L. *be flourished*, fr. *florere* to flourish] (1843): a period of flourishing (as of a person or movement)

**floss** \flās, flōs/ **n** [prob. modif. of *Flos* soft, weak (of silk fiber), fr. Gascon, fr. L. *fluxus*, lit., loose, flowing, pp. of *fluere* to flow — more at **FLUID**] (1759) **1** **a**: soft thread of silk or mercerized cotton for embroidery **b**: DENTAL FLOSS **2**: fluffy fibrous material

**floss** **vi** (1974): to use dental floss on ~ **vi**: to use dental floss  
**flossy** \flā-sē, flō-/ **adj** **floss-ier**, -est (1839) **1**: of, relating to, or having the characteristics of floss **2**: stylish or glamorous esp. at first impression (~ new hotels) — **floss-ily** \flā-sē-ē/ **adv**

**float** \flō-tā/ **n** [Sp.] (1527): a fleet of Spanish ships  
**floatation** \flō-tā-shān/ **n** [float] (1806) **1**: the act, process, or state of floating **2**: an act or instance of financing (as an issue of stock) **3**: the separation of the particles of a mass of pulverized ore according to their relative capacity for floating on a given liquid; also: any of various similar processes involving the relative capacity of materials for floating **4**: the ability (as of a tire or snowshoes) to stay on the surface of soft ground or snow

**float-la** \flō-ti-lā/ **n** [Sp. dim. of *flota* fleet, fr. OF *flote*, fr. ON *floti*; akin to OE *flota* ship, fleet — more at **FLAOT**] (1711) **1**: a fleet of ships or boats; esp.: a navy organizational unit consisting of two or more squadrons of small warships **2**: an indefinite large number (a ~ of changes)

**float-sam** \flāt-səm/ **n** [AF *floteson*, fr. OF *floter* to float, of Gmc origin; akin to OE *flotan* to float, *flota* ship] (ca. 1607) **1**: floating wreckage of a ship or its cargo; broadly: floating debris **2** **a**: a floating population (as of emigrants or castaways) **b**: an accumulation of miscellaneous or unimportant stuff

**flounce** \flaun(t)s/ **vi** **floounced**; **flounce-ing** [perh. of Scand origin; akin to Norw. *flunsa* to hurry] (1542) **1** **a**: to move with exaggerated jerky or bouncy motions (*floounced* about the room, jerking her shoulders, gesticulating — Agatha Christie); also: to move so as to draw attention to oneself (*floounced* into the lobby) **b**: to go with sudden determination (*floounced* out of the room in a huff) **2**: FLOUNDER, STRUGGLE

**flounce** **n** (1583): an act or instance of floouncing — **flouncy** \flaun(t)-sē/ **adj**

**flounce** **vi** **floounced**; **flounce-ing** [alter. of earlier *frounce*, fr. ME *frouncen* to curl] (1711): to trim with flounces

**flounce** **n** (1713): a strip of fabric attached by one edge; also: a wide ruffle — **flouncy** \flaun(t)-sē/ **adj**

**floouncing** \flaun(t)-sē/ **n** (1865): material used for flounces  
**floUNDER** \flaun-dər/ **n**, **pl** **flounders** or **flounders** [ME, fr. AF *floundre*, of Scand origin; akin to ON *flythra* flounder] (15c): FLATFISH; esp.: a fish of either of two families (Pleuronectidae and Bothidae) that include important marine food fishes

**flounder** **vi** **floundered**; **flound-er-ing** \d-(ə)-rē/ [prob. alter. of *founder*] (1592) **1**: to struggle to move or obtain footing: thrash about wildly **2**: to proceed or act clumsily or ineffectually

**flour** \flaur/ **n** [ME — more at **FLOWER**] (13c) **1**: finely ground meal of wheat usu. largely freed from bran; also: a similar meal of another material (as a cereal grain, an edible seed, or dried processed fish) **2**: a fine soft powder — **flour-less** **adj** — **floury** \-ē/ **adj**

**flour** **vi** (ca. 1657): to coat with or as if with flour ~ **vi**: to break up into particles

**flour-ish** \flār-ish, flā-nish/ **vb** [ME *florishen*, fr. MF *floriss-*, stem of *florir*, fr. (assumed) *\*L. florire*, alter. of *L. florere*, fr. *flor-*, *flas* flower] **vi** (14c) **1**: to grow luxuriantly; **THRIVE** **2** **a**: to achieve success: PROSPER **b**: to be in a state of activity or production (~ed around 1850) **c**: to reach a height of development or influence **3**: to make bold and sweeping gestures ~ **vi**: to wield with dramatic gestures: BRANDISH **syn** see **SWING** — **flour-ish-er** **n** — **flour-ish-ingly** \-i-shē-ē/ **adv**

**flourish** **n** (1597) **1** **a**: a period of thriving **b**: a luxuriant growth or profusion (a ~ of white hair) (a springtime ~ of color) **2** **a**: a florid bit of speech or writing (rhetorical ~es) **b**: an ornamental stroke in writing or printing **c**: a decorative or finishing detail (a house with clever little ~es) **3**: FANFARE **4**: an act or instance of brandishing or waving **5**: showiness in the doing of something (opened the door with a ~) **6**: a sudden burst (as of activity) (the week ends with a ~ of tests)

**flout** \flaut/ **vb** [prob. fr. ME *flouten* to play the flute, fr. *floute* flute] **vi** (1551) **1**: to indulge in scornful disregard: SCORN (~ing the rules) ~ **vi**: to indulge in scornful behavior **syn** see **SCOFF** **usage** see **FLAUNT** — **flout-er** **n**

**flout** **n** (ca. 1570): JEER

**flow** \flō/ **vb** [ME, fr. OE *flōwan*; akin to OHG *flouwen* to rinse, wash, *L. pluer* to rain, *Gk. plein* to sail, float] **vi** (bef. 12c) **1** **a**: (1): to issue or move in a stream (2): CIRCULATE **b**: to move with a continual change of place among the constituent particles (molasses ~s slowly) **2**: RISE (the tide ebbs and ~s) **3**: AROUND **4** **a**: to proceed smoothly and readily (conversation ~ed easily) **b**: to have a smooth continuity **5**: to hang loose and billowing **6**: to derive from a source: COME (the wealth that ~s from trade) **7**: to deform under stress without cracking or rupturing — used esp. of minerals and rocks **8**: MENSTRUATE ~ **vi** **1**: to cause to flow **2**: to discharge in a flow **syn** see **SPRING** — **flow-ing-ly** \-ē-ē/ **adv**

**flow** **n** (15c) **1**: an act of flowing **2**: FLOOD **la**, **2**, **3** **a**: a smooth uninterrupted movement or progress (a ~ of information) **b**: STREAM; also: a mass of material which has flowed when molten (an old lava ~) **c**: the direction of movement or development (go with the ~) **4**: the quantity that flows in a certain time **5**: MENSTRUATION **6**: the motion characteristic of fluids **b**: a continuous transfer of energy

**flow-age** \flō-ij/ **n** (1830) **1** **a**: an overflowing onto adjacent land **b**: a body of water formed by overflowing or damming **c**: floodwa-

ter esp. of a stream **2**: gradual deformation of a body of (as rock) by intermolecular shear

**flow-chart** \flō-čārt/ **n** (1920): a diagram that shows step progression through a procedure or system esp. using connect a set of conventional symbols — **flow-chart-ing** \flō-čārt-ē/ **n**  
**flow cy-to-m-e-try** \flō-si-tā-mā-trē/ **n** (1978): a technique using and sorting cells and their components (as DNA) by a fluorescent dye and detecting the fluorescence usu. by illumination

**flow diagram** **n** (1943): FLOWCHART

**flower** \flau(-ə)-r/ **n** [ME *flour* flower, best of anything, flour, fr. OF *flor*, flour, fr. L. *flor-*, *flor-* — more at **BLOW**] (13c) **1** **a**: BLOSSOM, INFLORESCENCE **b**: a shoot of the sporophyte of a higher plant that is modified for reproduction and consists of a shortened axis bearing modified leaves; esp.: one of a seed plant differentiated into a calyx, corolla, stamens, and carpels **c**: a plant cultivated for its blossoms **2** **a**: the best part or example (the ~ of our youth) **b**: the finest most vigorous period **c**: a state of blooming or flourishing (in full ~) **3** **pl**: a finely divided powder produced esp. by condensation or sublimation (~s of sulfur) — **flower-ed** \flau(-ə)-rd/ **adj** — **flower-ful** \flau(-ə)-fəl/ **adj** — **flower-less** \-ləs/ **adj** — **flower-like** \-līk/ **adj**

**flower** **vi** (13c) **1** **a**: DEVELOP (~ed into young woman) **b**: FLOURISH **2**: to produce flowers: BLOSSOM ~ **vi** **1**: to bear flowers **2**: to decorate with flowers or floral designs — **er** \flau(-ə)-r-ē/ **n**

**flower-age** \flau(-ə)-r-ij/ **n** (1840): a flowering process, station

**flower bud** **n** (1828): a plant bud that produces only a flower  
**flower bug** **n** (ca. 1889): any of various small mostly black predaceous bugs (family Anthrenidae) that frequent flowers on pest insects (as aphids and thrips)

**flower child** **n** (1967): a hippie who advocates love, beauty, flower-er also **flower-ette** \flau(-ə)-r-ēt/ **n** (15c): FLORET **1**: flower girl **2**: a little girl who carries flowers at a wedding  
**flower head** **n** (1845): a capitulum (as of a composite) having flowers so arranged that the whole inflorescence looks like a flower

**flowering dogwood** **n** (1843): a common spring-flowering bracted dogwood (*Cornus florida*)

**flowering plant** **n** (1745): ANGIOSPERM

**flower people** **n** **pl** (1967): FLOWER CHILDREN

**flower-pot** \flau(-ə)-pāt/ **n** (1598): a pot in which to grow flower-ery \flau(-ə)-r-ē/ **adj** (14c) **1**: of, relating to, or resembling **2**: marked by or given to rhetorical elegance — **flou(-ə)-r-ē-ly** **adv** — **flower-i-ness** **n**

**flow-meter** \flō-mē-tər/ **n** (1915): an instrument for measuring more properties (as velocity or pressure) of a flow (as of a pipe)

**flown** \flōn/ **past part** of **FLY**

**flown** **adj** [archaic pp. of *flow*] (1626): filled to excess  
**flow sheet** **n** (1912): FLOWCHART

**flow-stone** \flō-stōn/ **n** (1925): calcite deposited by a thin flowing water usu. along the walls or floor of a cave

**flu** \flū/ **n** [by shortening] (1839) **1**: INFLUENZA **2**: any virus diseases marked esp. by respiratory symptoms

**flub** \flab/ **vb** **flubbed**; **flub-bing** [origin unknown] **vi** (18c) make a mess of: BOTCH (*flubbed* my lines) ~ **vi**: BLUNDER

**flub** **n** (1948): an act or instance of flubbing  
**flub-dub** \flab-dəb/ **n** [origin unknown] (1888): BUNKUM, DASH

**fluc-tu-ant** \flak-čə-want/ **adj** (1560) **1**: moving in waves: ABLE, UNSTABLE **3**: being movable and compressible (a ~able fluc-tu-ate \flak-čə-wāt/ **vb** -at-ed, -at-ing [L. *fluctuare*, fr. *fluctus* flow, wave, fr. *fluere* — more at **FLUID**] **vi**: to shift back and forth uncertainly **2**: to ebb and flow in ~ **vi**: to cause to fluctuate **syn** see **SWING** — **fluc-tu-a-tion** \flū-šən/ **n** — **fluc-tu-a-tion-al** \flū-šə-nəl, -shə-nəl/ **adj**

**flue** \flū/ **n** [origin unknown] (1582): an enclosed passage directing a current: as **a**: a channel in a chimney for conveying smoke to the outer air **b**: a pipe for conveying flame gases around or through water in a steam boiler **c**: an air leading to the lip of a wind instrument **d**: FLUE PIPE

**flue-cured** \flū-kyurd/ **adj** (1905): cured with heat transmitted a flue without exposure to smoke or fumes (~ tobacco)

**flu-en-cy** \flū-ən(t)-sē/ **n** (1636): the quality or state of being **flu-ent** \flū-ənt/ **adj** [L. *fluens*, prp. of *fluere*] (1599) **1**: capable of flowing: FLUID **b**: capable of moving with ease (~ the ~ body of a dancer) **2** **a**: ready or facile in speech (~ ish) **b**: effortlessly smooth and rapid: POLISHED (a ~ performer) — **flu-ent-ly** **adv**

**flue pipe** **n** (1852): an organ pipe whose tone is produced by current striking the lip and causing the air within to vibrate — **pare** REED PIPE

**flue stop** **n** (1855): an organ stop made up of flue pipes

**fluff** \flaf/ **n** [perh. blend of *fluff* (fluff) and *puff*] (1790) **1**: DOWN **2**: something fluffy **3**: something inconsequential **4**: DER; esp.: an actor's lapse of memory

**fluff** **vi** (1875) **1**: to become fluffy **2**: to make a mistake, forget or bungle one's lines in a play ~ **vi** **1**: to make fluff: to spoil by a mistake: BOTCH **b**: to deliver badly or (for lines) in a play

**fluffy** \flā-fē/ **adj** **fluff-ier**, -est (ca. 1825) **1** **a**: covered or resembling fluff **b**: being light and soft or airy (a ~ coat)



cross section of fl  
 filament, 2 anther,  
 style, 5 petal, 6 ovary,  
 8 pedicel, 7 stamen,  
 11 perianth.

flute 1b

ʌ abut ʌ kitten, F table ʌʌ further ʌʌ ash ʌʌ ace ʌʌ mop, mar  
 ʌʌ out ʌʌ chin ʌʌ bet ʌʌ easy ʌʌ go ʌʌ hit ʌʌ ice ʌʌ job  
 ʌʌ sing ʌʌ go ʌʌ law ʌʌ boy ʌʌ thin ʌʌ the ʌʌ loot ʌʌ foot  
 ʌʌ yet ʌʌ vision ʌ, k, ʌ, æ, œ, ʌ see Guide to Pronunciation

# STATISTICAL MECHANICS

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HARPER & ROW  
Publishers  
New York Evanston San Francisco London

Sponsoring Editor: John A. Woods  
Project Editor: Ralph Cato  
Designer: T. R. Funderburk  
Production Supervisor: Will C. Jomarrón  
Compositor: Santype International Ltd.  
Printer/Binder: Halliday Lithograph Corporation  
Art Studio: Vantage Art, Inc.

STATISTICAL MECHANICS

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Library of Congress Cataloging in Publication Data  
McQuarrie, Donald Allan.  
Statistical mechanics.

(Harper's chemistry series)

"Portions of this work were originally published under the title: Statistical thermodynamics."

Bibliography: p.

Includes index.

1. Statistical mechanics. 2. Statistical thermodynamics. I. Title.

QC174.8.M3 530.1'32 75-20499  
ISBN 06-044366-9

# KINETIC THEORY OF GASES AND THE BOLTZMANN EQUATION

In Section 7-2 we introduced the concept of phase space and distribution functions in phase space. We also derived the Liouville equation, which is the equation of motion that the phase space distribution function must satisfy. Since we were interested only in equilibrium statistical mechanics at that time, we did not consider the Liouville equation in any detail. In this chapter we shall review the concept of phase space and derive the Liouville equation again. We shall then introduce reduced distribution functions and derive the Bogoliubov, Born, Green, Kirkwood, Yvon (BBGKY) hierarchy. This hierarchy is the nonequilibrium generalization of the Kirkwood integral equation hierarchy for the fluid distribution functions,  $g^{(n)}(\mathbf{r}_1, \dots, \mathbf{r}_n)$ , of Chapter 13. Nobody has yet devised a successful way to uncouple the BBGKY hierarchy, and so in Section 18-4 we shall derive a physical, yet approximate, equation for the distribution function for gases. This equation, called the Boltzmann equation, is the central equation of the rigorous kinetic theory of gases. In Section 18-5, we shall derive some of the general consequences of the Boltzmann equation that can be determined without actually solving it completely. We shall discuss its solution in Chapter 19. The standard reference for most of this chapter is Hirschfelder, Curtiss, and Bird. Mazo (in "Additional Reading") also discusses these topics well.

## 18-1 PHASE SPACE AND THE LIOUVILLE EQUATION

Consider a system of  $N$  point particles. The classical dynamical state of this system is specified by the  $3N$  momentum components  $p_1, p_2, \dots, p_{3N}$  and the  $3N$  spatial coordinates  $q_1, \dots, q_{3N}$ . We can construct a  $6N$ -dimensional space whose coordinates are  $q_1, q_2, \dots, p_1, \dots, p_{3N}$ . One point in this *phase space* completely specifies the microscopic dynamical state of our  $N$ -particle system. As the system evolves in time, this *phase point* moves through phase space in a manner completely dictated by the equations of motion of the system. Actually, one never knows (nor really cares to know) the  $6N$  coordinates of a macroscopic system. Rather, one knows just a few

macroscopic mechanical properties of the system, such as the energy, volume, velocity, etc. Clearly there are a great number of points in phase space that are compatible with the few variables that we know about the system. The set of all such phase points constitutes an *ensemble of systems*. The number of systems in an ensemble approaches infinity, and so the set of phase points that could possibly represent our system becomes quite dense. This allows us to define a *density of phase points* or *distribution function* as the fraction of phase points contained in the volume  $dq_1 dq_2 \cdots dp_{3N}$ . We shall denote the phase space distribution function by  $f_N(q_1, q_2, \dots, p_{3N}, t)$ , or more conveniently by  $f_N(p, q, t)$ . We shall often use this abbreviated notation. Similarly, we shall often denote  $dq_1, dq_2 \cdots dp_{3N}$  by  $dp dq$ . The density  $f_N(p, q, t)$  is normalized such that

$$\int f_N(p, q, t) dp dq = 1$$

Since each phase point moves in time according to the equations of motion of the system it describes,  $f_N$  itself must obey some sort of equation of motion. The equation that  $f_N(p, q, t)$  satisfies can be readily determined by using the methods of the previous chapter, particularly, the argument associated with Eqs. (17-1) to (17-5). The number of phase points within some arbitrary volume  $v$  is

$$n = \mathcal{N} \int_v f_N(p, q, t) dp dq$$

where we are using the condensed notation of letting  $p$  and  $q$  denote all the spatial coordinates and momenta necessary to specify a system in the ensemble. The rate of change of the number of phase points within  $v$  is

$$\frac{dn}{dt} = \mathcal{N} \int_v \frac{\partial f_N}{\partial t} dp dq \quad (18-1)$$

Since phase points are neither created nor destroyed, the rate of change of  $n$  must be given by the rate at which phase points flow through the surface enclosing  $v$ . The rate of flow of phase points is  $\mathcal{N} f_N \mathbf{u}$ , where  $\mathbf{u}$  is not just the  $3N$ -dimensional vector  $(\dot{q}_1, \dot{q}_2, \dots, \dot{q}_{3N})$ , but the  $6N$ -dimensional vector  $(\dot{q}_1, \dots, \dot{p}_1, \dots, \dot{p}_{3N})$  since the spatial coordinates and momenta play an equivalent role in phase space. We integrate this flow over the surface to get

$$\frac{dn}{dt} = -\mathcal{N} \int_S f_N \mathbf{u} \cdot d\mathbf{S}$$

The negative sign here indicates that an outflow of phase points yields a negative value for  $dn/dt$  since  $\mathbf{u} \cdot d\mathbf{S}$  is positive if  $\mathbf{u}$  is directed outward from  $v$  and negative if  $\mathbf{u}$  is directed inward.

The surface integral can be transformed to a volume integral by using Gauss' theorem to get

$$\frac{dn}{dt} = -\mathcal{N} \int_v \nabla \cdot (f_N \mathbf{u}) dp dq \quad (18-2)$$

If we subtract Eq. (18-1) from Eq. (18-2) and realize that this equation is valid for any choice of  $v$ , we have the equation for the conservation of phase points

$$\frac{\partial f_N}{\partial t} + \nabla \cdot (f_N \mathbf{u}) = 0 \quad (18-3)$$



in which it should be clear that since we are dealing with phase space

$$\mathbf{u} = (\dot{q}_1, \dots, \dot{q}_{3N}, \dot{p}_1, \dots, \dot{p}_{3N})$$

and

$$\begin{aligned} \nabla \cdot f_N \mathbf{u} &= \sum_{j=1}^{3N} \frac{\partial}{\partial q_j} (f_N \dot{q}_j) + \sum_{j=1}^{3N} \frac{\partial}{\partial p_j} (f_N \dot{p}_j) \\ &= \sum_{j=1}^{3N} \left\{ \frac{\partial f_N}{\partial q_j} \dot{q}_j + \frac{\partial f_N}{\partial p_j} \dot{p}_j \right\} + \sum_{j=1}^{3N} \left\{ \frac{\partial \dot{q}_j}{\partial q_j} + \frac{\partial \dot{p}_j}{\partial p_j} \right\} f_N \end{aligned}$$

But Eq. (7-27) shows that the summand of the second summation here is zero, and so Eq. (18-3) becomes

$$\frac{\partial f_N}{\partial t} + \sum_{j=1}^{3N} \frac{\partial f_N}{\partial q_j} \dot{q}_j + \sum_{j=1}^{3N} \frac{\partial f_N}{\partial p_j} \dot{p}_j = 0 \quad (18-4)$$

Using Hamilton's equations of motion,

$$\dot{p}_i = -\frac{\partial H}{\partial q_i} \quad \text{and} \quad \dot{q}_i = \frac{\partial H}{\partial p_i}$$

Eq. (18-4) can be written

$$\frac{\partial f_N}{\partial t} + \sum_{j=1}^{3N} \left( \frac{\partial H}{\partial p_j} \frac{\partial f_N}{\partial q_j} - \frac{\partial H}{\partial q_j} \frac{\partial f_N}{\partial p_j} \right) = 0 \quad (18-5)$$

The summation here is called a Poisson bracket and is commonly denoted by  $\{H, f_N\}$ ; so Eq. (18-5) is often written as

$$\frac{\partial f_N}{\partial t} + \{H, f_N\} = 0 \quad (18-6)$$

This is the Liouville equation, the most fundamental equation of statistical mechanics. In fact, it can be shown that the Liouville equation is equivalent to the  $6N$  Hamilton equations of motion of the  $N$ -body system.\*

In Cartesian coordinates, the Liouville equation reads

$$\frac{\partial f_N}{\partial t} + \sum_{j=1}^N \frac{\mathbf{p}_j}{m_j} \cdot \nabla_{\mathbf{r}_j} f_N + \sum_{j=1}^N \mathbf{F}_j \cdot \nabla_{\mathbf{p}_j} f_N = 0 \quad (18-6')$$

In this equation  $\nabla_{\mathbf{r}_j}$  denotes the gradient with respect to the spatial variables in  $f_N$ ;  $\nabla_{\mathbf{p}_j}$  denotes the gradient with respect to the momentum variables in  $f_N$ ; and  $\mathbf{F}_j$  is the total force on the  $j$ th particle.

One often sees the Liouville equation written as

$$i \frac{\partial f_N}{\partial t} = L f_N \quad (18-7)$$

where  $L$  is the Liouville operator,

$$L = -i \left( \sum_{j=1}^N \frac{\mathbf{p}_j}{m_j} \cdot \nabla_{\mathbf{r}_j} + \sum_{j=1}^N \mathbf{F}_j \cdot \nabla_{\mathbf{p}_j} \right) \quad (18-8)$$

\* Mazo, "Additional Reading," p. 23; M. Beran, *Amer. J. Phys.*, 35, p. 242, 1967.

The Liouville operator has been defined in such a way as to bring the Liouville equation into the form of the Schrödinger equation. A formal, and sometimes useful, solution to Eq. (18-7) is

$$f_N(\mathbf{p}, \mathbf{r}, t) = e^{-iLt} f_N(\mathbf{p}, \mathbf{r}, 0) \quad (18-9)$$

Note that the operator  $\exp(-iLt)$  displaces  $f_N$  ahead a distance  $t$  in time. This operator is called the time displacement operator of the system.

## 18-2 REDUCED DISTRIBUTION FUNCTIONS

Once we have the distribution function  $f_N(p, q, t)$ , we may compute the ensemble average of any dynamical variable,  $A(p, q, t)$ , from the equation

$$\langle A(t) \rangle = \int A(p, q, t) f_N(p, q, t) dp dq \quad (18-10)$$

It turns out that the dynamical variables of interest are functions of either the coordinates and momenta of just a few particles or can be written as a sum over such functions. A familiar example of this is the total intermolecular potential of the system. To a good approximation, this can be written as a sum over pair-wise potentials, and so

$$\langle U \rangle = \sum_{i,j} \int \cdots \int u(\mathbf{r}_i, \mathbf{r}_j) f_N(\mathbf{r}_1, \dots, \mathbf{p}_N, t) d\mathbf{r}_1 \cdots d\mathbf{p}_N \quad (18-11)$$

We encountered similar integrands when we studied the equilibrium theory of liquids. There we integrated over the coordinates of all the particles except  $i$  and  $j$  and called the resulting function of  $\mathbf{r}_i$  and  $\mathbf{r}_j$  a radial distribution function. We do the same thing here. We define reduced distribution functions  $f_N^{(n)}(\mathbf{r}_1, \dots, \mathbf{r}_n, \mathbf{p}_1, \dots, \mathbf{p}_n, t)$  by

$$f_N^{(n)}(\mathbf{r}_1, \dots, \mathbf{r}_n, \mathbf{p}_1, \dots, \mathbf{p}_n, t) = \frac{N!}{(N-n)!} \int \cdots \int f_N(\mathbf{r}_1, \dots, \mathbf{p}_N, t) d\mathbf{r}_{n+1} \cdots d\mathbf{r}_N d\mathbf{p}_{n+1} \cdots d\mathbf{p}_N \quad (18-12)$$

We shall usually drop the  $N$  subscript and furthermore write this simply as  $f^{(n)}(\mathbf{r}^n, \mathbf{p}^n, t)$ . Usually only  $f^{(1)}$  and  $f^{(2)}$  are necessary, and therefore we want to derive an equation for  $f^{(1)}$  and  $f^{(2)}$ . To do this, write the force  $\mathbf{F}_j$  appearing in the Liouville equation as the sum of the forces due to the other molecules in the system  $\sum_i \mathbf{F}_{ij}$  and an external force  $\mathbf{X}_j$ . Then multiply through by  $N!/(N-n)!$  and integrate over  $d\mathbf{r}_{n+1} \cdots d\mathbf{r}_N d\mathbf{p}_{n+1} \cdots d\mathbf{p}_N$  to get (Problem 18-2)

$$\begin{aligned} \frac{\partial f^{(n)}}{\partial t} + \sum_{j=1}^n \frac{\mathbf{p}_j}{m_j} \cdot \nabla_{\mathbf{r}_j} f^{(n)} + \sum_{j=1}^n \mathbf{X}_j \cdot \nabla_{\mathbf{p}_j} f^{(n)} \\ + \frac{N!}{(N-n)!} \sum_{i,j=1}^n \int \cdots \int \mathbf{F}_{ij} \cdot \nabla_{\mathbf{p}_j} f d\mathbf{r}_{n+1} \cdots d\mathbf{r}_N d\mathbf{p}_{n+1} \cdots d\mathbf{p}_N = 0 \end{aligned} \quad (18-13)$$

We have used the fact that  $f$  vanishes outside the walls of the container and when  $\mathbf{p}_i = \pm \infty$ . The last term in Eq. (18-13) can be broken up into two parts:

$$\begin{aligned} \sum_{i,j=1}^n \mathbf{F}_{ij} \cdot \nabla_{\mathbf{p}_j} f^{(n)} \\ + \frac{N!}{(N-n)!} \sum_{j=1}^n \sum_{i=n+1}^N \int \cdots \int \mathbf{F}_{ij} \cdot \nabla_{\mathbf{p}_j} f d\mathbf{r}_{n+1} \cdots d\mathbf{r}_N d\mathbf{p}_{n+1} \cdots d\mathbf{p}_N \end{aligned}$$

The second term here can be written as

$$\sum_{j=1}^n \iint \mathbf{F}_{j,n+1} \cdot \nabla_{\mathbf{p}_j} f^{(n+1)} d\mathbf{r}_{n+1} d\mathbf{p}_{n+1}$$

Putting all this together finally gives an exact equation for  $f^{(n)}$ , namely, (Problem 18-3),

$$\begin{aligned} \frac{\partial f^{(n)}}{\partial t} + \sum_{j=1}^n \frac{\mathbf{p}_j}{m_j} \cdot \nabla_{\mathbf{r}_j} f^{(n)} + \sum_{j=1}^n \mathbf{X}_j \cdot \nabla_{\mathbf{p}_j} f^{(n)} \\ + \sum_{i,j=1}^n \mathbf{F}_{ij} \cdot \nabla_{\mathbf{p}_j} f^{(n)} + \sum_{j=1}^n \iint \mathbf{F}_{j,n+1} \cdot \nabla_{\mathbf{p}_j} f^{(n+1)} d\mathbf{r}_{n+1} d\mathbf{p}_{n+1} = 0 \end{aligned} \quad (18-14)$$

This is the so-called Bogoliubov, Born, Green, Kirkwood, Yvon (BBGKY) hierarchy. This is the time-dependent generalization of the hierarchy that we derived earlier in the equilibrium theory of fluids. In fact, if one assumes that

$$f^{(n)} = g^{(n)}(\mathbf{r}_1, \dots, \mathbf{r}_n) \exp\left\{-\frac{1}{2mkT} \sum_{j=1}^n p_j^2\right\}$$

multiplies Eq. (18-14) through by  $p_i$ ,  $1 \leq i \leq n$ , and integrates over all momenta, one obtains the equilibrium hierarchy for  $g^{(n)}(\mathbf{r}_1, \dots, \mathbf{r}_n)$  (Problem 18-4). It would seem natural at this point to truncate this hierarchy by some sort of a superposition approximation, but so far this approach has not been successful.\* We shall end up deriving approximate equations for  $f^{(1)}$  and  $f^{(2)}$ .

Everything we have done up to now has been independent of density; i.e., it has been applicable to any density. Now we shall specialize to systems of dilute gases.

### 18-3 FLUXES IN DILUTE GASES

In a dilute gas, most of the molecules are not interacting with any other molecule and are just traveling along between collisions. Because of this, the macroscopic properties of a gas depend upon only the singlet distribution function  $f_j^{(1)}(\mathbf{r}, \mathbf{p}_j, t)$ . The subscript  $j$  here denotes the singlet distribution function of species  $j$ . This is the central distribution function of any theory of transport in dilute gases. In this section we shall define a number of averages over  $f_j^{(1)}$  and derive molecular expressions for the important flux quantities in terms of integrals over  $f_j^{(1)}$ . Since we shall be concerned only with gases in this and the following sections, we shall drop the superscript (1) from here on. We shall also write our equations in velocity space rather than momentum space, and so the distribution function of interest becomes  $f_j(\mathbf{r}, \mathbf{v}_j, t)$ . We shall renormalize  $f_j$  such that the integral of this distribution function over all velocities is the number density of  $j$  particles at the point  $\mathbf{r}$  at time  $t$ , i.e.,

$$\rho_j(\mathbf{r}, t) = \int f_j(\mathbf{r}, \mathbf{v}_j, t) d\mathbf{v}_j \quad (18-15)$$

Furthermore, if  $N_j$  is the total number of  $j$  molecules in our system, then

$$N_j = \iint f_j(\mathbf{r}, \mathbf{v}_j, t) d\mathbf{r} d\mathbf{v}_j \quad (18-16)$$

We shall now define a number of important average velocities.  $\mathbf{v}_j$  is the *linear*

\* See, for example, R. G. Mortimer, *J. Chem. Phys.*, 48, p. 1023, 1968.

velocity of a molecule of species  $j$ ; i.e., it is the velocity with respect to a coordinate system fixed in space. The average velocity is given by

$$\mathbf{v}_j(\mathbf{r}, t) = \frac{1}{\rho_j} \int \mathbf{v}_j f(\mathbf{r}, \mathbf{v}_j, t) d\mathbf{v}_j \quad (18-17)$$

and represents the macroscopic flow of species  $j$ . The *mass average velocity* is defined by

$$\mathbf{v}_0(\mathbf{r}, t) = \frac{\sum_j m_j \rho_j \mathbf{v}_j}{\sum_j m_j \rho_j} \quad (18-18)$$

Note that the denominator here is the mass density  $\rho_m(\mathbf{r}, t)$ . This velocity is often called the *flow velocity* or *stream velocity*. The momentum density of the gas is the same as if all the molecules were moving with velocity  $\mathbf{v}_0$ . The *peculiar velocity* is the velocity of a molecule relative to the flow velocity. The peculiar velocity  $\mathbf{V}_j$  is

$$\mathbf{V}_j = \mathbf{v}_j - \mathbf{v}_0 \quad (18-19)$$

The average of this peculiar velocity is the *diffusion velocity* (Problem 18-5). Clearly,

$$\bar{\mathbf{V}}_j = \frac{1}{\rho_j} \int (\mathbf{v}_j - \mathbf{v}_0) f_j(\mathbf{r}, \mathbf{v}_j, t) d\mathbf{v}_j \quad (18-20)$$

It is easy to show that (Problem 18-6)

$$\sum_j \rho_j m_j \bar{\mathbf{V}}_j = 0 \quad (18-21)$$

When we studied the elementary kinetic theory of gases, we saw that the various transport coefficients were related to molecular transport of mass, momentum, and kinetic energy. Let these molecular properties be designated collectively by  $\psi_j$ , where  $j$  refers to the particular species. We now derive expressions for the fluxes of these properties. Figure 18-1 shows a surface  $dS$  moving with velocity  $\mathbf{v}_0$ . The quantity  $\mathbf{n}$  is a unit vector normal to  $dS$ , and  $dS = \mathbf{n} dS$ . All the molecules that have velocity  $\mathbf{V}_j = \mathbf{v}_j - \mathbf{v}_0$  and that cross  $dS$  in the time interval  $(t, t + dt)$  must have been in a cylinder of length  $|\mathbf{V}_j| dt$  and base  $dS$ . This cylinder is shown in Fig. 18-1 and has a volume  $(\mathbf{n} \cdot \mathbf{V}_j) dS dt$ . Since there are  $f_j d\mathbf{v}_j$  molecules per unit volume with relative velocity  $\mathbf{V}_j$ , the number of  $j$  molecules that cross  $dS$  in  $dt$  is given by

$$(f_j d\mathbf{v}_j)(\mathbf{n} \cdot \mathbf{V}_j) dS dt$$

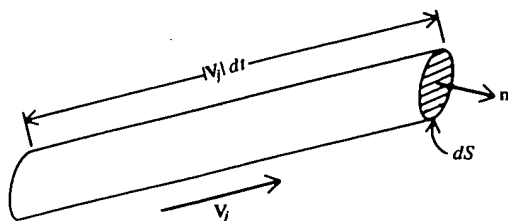


Figure 18-1. The cylinder containing all those molecules of species  $j$  with velocity  $\mathbf{V}_j$ , which cross the surface  $dS$  during the time interval  $dt$ . (From J. O. Hirschfelder, C. F. Curtiss, and R. B. Bird, *Molecular Theory of Gases and Liquids*. New York: Wiley, 1954.)

If each molecule carries with it a property  $\psi_j$ , then the flux of this property is

$$\psi_j f_j (\mathbf{n} \cdot \mathbf{V}_j) d\mathbf{v}_j$$

and the total flux across this surface is

$$\text{total flux} = \int \psi_j f_j (\mathbf{n} \cdot \mathbf{V}_j) d\mathbf{v}_j = \mathbf{n} \cdot \int \psi_j f_j \mathbf{V}_j d\mathbf{v}_j = \mathbf{n} \cdot \boldsymbol{\psi}_j \quad (18-22)$$

The vector  $\boldsymbol{\psi}_j$ ,

$$\boldsymbol{\psi}_j = \int \psi_j f_j \mathbf{V}_j d\mathbf{v}_j \quad (18-23)$$

is called the flux vector associated with the property  $\psi_j$ . The component of this vector in any direction is the transport of the property  $\psi_j$  in that direction. Let us now consider the various examples of  $\boldsymbol{\psi}_j$ .

#### TRANSPORT OF MASS

In this case,  $\psi_j = m_j$ , and

$$\boldsymbol{\psi}_j = m_j \int f_j \mathbf{V}_j d\mathbf{v}_j = \rho_j m_j \overline{\mathbf{V}_j} \equiv \mathbf{j}_j \quad (18-24)$$

#### TRANSPORT OF MOMENTUM

Here  $\psi_j = m_j V_{jx}$ , and

$$\boldsymbol{\psi}_j = m_j \int V_{jx} f_j \mathbf{V}_j d\mathbf{v}_j = \rho_j m_j \overline{V_{jx} \mathbf{V}_j} \quad (18-25)$$

which is the flux of the  $x$ -component of momentum relative to  $\mathbf{v}_0$ . The flux of momentum is a pressure, which has components

$$(p_j)_{xx} = \rho_j m_j \overline{V_{jx} V_{jx}}$$

$$(p_j)_{xy} = \rho_j m_j \overline{V_{jx} V_{jy}}, \text{ etc}$$

or, in general,

$$p_j = \rho_j m_j \overline{\mathbf{V}_j \mathbf{V}_j} \quad (18-26)$$

which is the partial pressure tensor of the  $j$ th species.

#### TRANSPORT OF KINETIC ENERGY

$$\psi_j = \frac{1}{2} m_j V_j^2$$

and

$$\boldsymbol{\psi}_j = \frac{m_j}{2} \int v_j^2 \mathbf{V}_j f_j d\mathbf{v}_j = \frac{1}{2} \rho_j m_j \overline{V_j^2 \mathbf{V}_j} = \mathbf{q}_j \quad (18-27)$$

the heat flux vector of the  $j$ th species.

It should be clear at this point that once we have an expression for  $f_j(\mathbf{r}, \mathbf{v}_j, t)$ , we can calculate all the fluxes and hence all the transport properties of a dilute gas. What we need now is  $f_j$ , or at least an equation that gives  $f_j$  as its solution. The only equation we have up to now is Eq. (18-14) with  $n = 1$ , and it can be seen that this also contains  $f_j^{(2)}$ . As we said earlier, nobody has found a successful way to uncouple this system. In the next section we shall derive an equation for  $f_j$ , the Boltzmann equation, which is the fundamental equation of the rigorous kinetic theory of gases.

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